CRYSTAL STRUCTURE OF FROZEN CYCLOHEXANE AT $-180°C$*

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(*Received for publication, July* 22, 1958)

Plate XI

ABSTRACT. The Debye-Scherrer patterns of frozen cyclohexane at $-5°C$ and at $-180°C$ have been photographed and analysed. It has been found that the crystal at $-5°C$ is cubic with the edge of the unit cell $a = 8.80$ A.U. At $-180°C$ the crystal has been found to be monoclinic with the unit cell dimensions as $a = 8.82$ A.U., $b = 9.84$ A.U., $c = 15.90$ A.U. and $\beta = 109°$. The density of cyclohexane at $-180°C$ has been measured and the number of asymmetric molecules in the unit cell has been found to be 8. The space group C_s^3 has been assigned to the crystal.

INTRODUCTION

The crystal structure of cyclohexane was first studied by Hassel and Kringstad (1930) who found the crystal to belong to the cubic system with unit cell dimensions $a = 8.43$ A.U. They studied the Debye-Scherrer pattern of the substance at $-80°C$, by freezing the liquid with solid CO_2-acetone mixture. The crystal structure of the substance was re-examined by Hassel and Sommerfeldt (1938) at $-8°C$ and $-40°C$ and they also found the crystal to be cubic with $a = 8.76$ A.U. at both the temperatures. They further tried to determine the space group and concluded that the space group might be T_d^1. Lonsdale and Smith (1939) studied the crystal structure of the substance at $-180°C$ and reported that the powder pattern obtained by them did not correspond to any one of cubic, tetragonal or hexagonal lattices. They further pointed out that the crystal might have a low temperature modification of low symmetry or at that particular temperature two crystalline forms might have been present simultaneously. They used the results of the investigation by Hassel and Kringstad (1930) to find out the space group of the crystal at $-80°C$ and concluded that the space group might be either T_h^2 or O_h^4.

The structure of the crystal of cyclohexane at $-180°C$ was therefore not known. An attempt has been made to study the Debye-Scherrer pattern of the crystal at $-180°C$ and to compare it with that due to the crystal at $-5°C$ in

* Communicated by Prof. S. C. Sirkar.

order to find the space group to which the crystal at −180°C belongs. As shown below it has been found that the crystal at −180°C belongs to monoclinic system and the space group has also been determined.

TABLE I

Spacings of cyclohexane

Cubic form			Monoclinic form at −180°C		
Indices	Observed at −5°C	From the data of Hassel and Sommerfeldt (1938) at −40°C observed	Indices	Observed	Calculated from the proposed structure
111	5 08 (s)	5 06 (vs)	111	5 39 (ms)	5 39
			020	4 92 (vs)	4.92
			113	4.54 (w)	4.54
200	4.40 (m)	4.37 (vs)	200	4.17 (m)	4 17
210		3 93 (vw)	104	3.92 (vs)	3 94
211		3.62 (w)	004	3.76 (m)	3.76
			122, 211	3 46 (w)	3.46
220		3 14 (vw)	202, 222	3 22 (w)	3.22
			124, 104	3.09 (vw)	3.08
300, 221		2.93 (ms)	$30\bar{2}$	2 94 (vw)	2.94
310		2.82 (vw)	300	2 77 (m)	2.78
311	2 65 (vw)	2 65 (vw)	$10\bar{6}$	2 66 (m)	2 655
222		2.54 (w)	006	2 515 (w)	2.51
321		2.30 (vw)	040	2.45 (m)	2.46
400		2.23 (w)	404	2 15 (w)	2 15
411, 330		2.09 (w)	044	2 06 (m)	2.06
421		1.93 (vw)	051, $40\bar{6}$	1.94 (w)	1.94
			308	1 87 (w)	1.87
			340	1.84 (vw)	1 84
			060	1.64 (m)	1.64
			128	1 62 (vw)	1.62
			520	1.57 (vw)	1.58
			$30\overline{10}$, 439	1.55 (vw)	1.55
			048	1.495 (w)	1.495
			453, 228	1.47 (vw)	1.464, 1.468

EXPERIMENTAL

Pure cyclohexane, distilled under low pressure, was used in obtaining the Debye-Scherrer patterns of the crystal. The photographs at −180°C were taken by the method described earlier (Krishna Murti and Sen, 1956) with the camera of special design (Biswas, 1958). The Dewar vessel was modified so as to allow only the liquid oxygen vapour to pass on the specimen in order to record the pattern at a temperature just below 0°C and the temperature obtained in this way was −5°C as shown by a thermometer.

A Seifert X-ray tube running at 32 KV, 26 ma. was used to photograph the patterns. The X-ray tube was provided with a copper target and a nickel filter was used to cut off the Kβ radiation. An exposure of about 3.5 hours was sufficient to record the patterns with moderate densities. The radius of the camera was measured by photographing a Debye-Scherrer pattern due to aluminium powder and was found to be 4.5 cms.

RESULTS AND DISCUSSION

The photographs of the Debye-Scherrer patterns obtained at different temperatures are reproduced in Plate XI. The spacings calculated from the Debye-Scherrer patterns of cyclohexane at different temperatures are given in Table I. The intensities of different rings in the patterns estimated visually are given along with the spacings as very strong (vs), strong (s), medium (m), weak (w) and very weak (vw).

It is found that the spacings obtained for the crystal at −5°C correspond to those of a cubic crystal with the edge $a = 8.80$ A.U. This is in confirmity with the results reported by earlier authors.

It can be easily seen from the patterns reproduced in Plate XI that the crystal structure of the substance at −180°C is quite different from that at −5°C. Attempts were made to analyse the pattern by the methods of Hesse (1948) and Lipson (1949) and it was found that the pattern does not correspond to cubic, tetragonal, hexagonal or orthorhombic system. Since it appears to belong to a lower symmetry it was assumed that it might belong to monoclinic symmetry, as it is the next in order of symmetry. A trial and error method was used and as the crystal belongs to a cubic system at −5°C, it was assumed that a distortion is produced in the crystalline lattice.

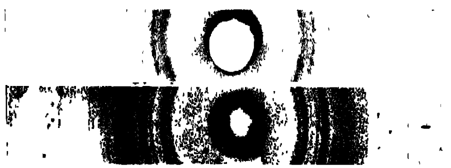
The spacings 4.92 A.U., 4.17 A.U. and 3.76 A.U. have been assigned to the indices (020), (200) and (004) and the spacing 5.39 then agrees with that of the plane (111), if $\beta = 109°$. The unit cell dimensions of the crystal calculated with the above data are $a = 8.82$ A.U., $b = 9.84$ A.U., $c = 15.90$ A.U. and $\beta = 109°$. By trial the indices of all the planes giving the lines in the pattern have been found. It can be seen from Table I that it has been possible to

Indian Journal of Physics, Vol. XXXII, No. 10.

PLATE XI

(a)

(b)



Debye-Scherrer patterns of solid cyclohexane

(a) Crystals at $-5°C$

(b) ,, ,, $-180°C$

assign indices to all the spacings and that the observed and calculated spacings agree closely with each other.

The density of frozen cyclohexane at −180°C was measured by the method used earlier in this laboratory (Biswas and Sirkar, 1957) and was found to be 0.8561. The number of molecules in the unit cell was calculated using this value of density and it was found to be 8. It can be seen from Table I that all the (hkl) spacings with (k+l) odd are absent. So the space group C_s^3 is ascribed to the crystal.

Hence it can be concluded that the crystal is cubic at −5°C but it has a low-temperature modification of lower symmetry at −180°C, the lattice at −180°C being monoclinic and the space group C_s^3.

ACKNOWLEDGMENT

The author is indebted to Professor S. C. Sirkar, D.Sc., F.N.I., for his kind interest and guidance during the progress of the work.

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